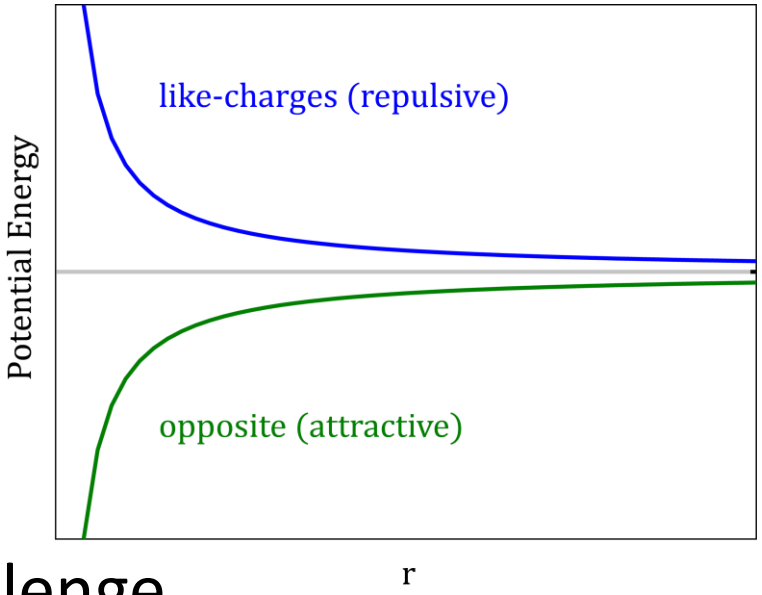
Previously missed topics, a collection

Electrostatics

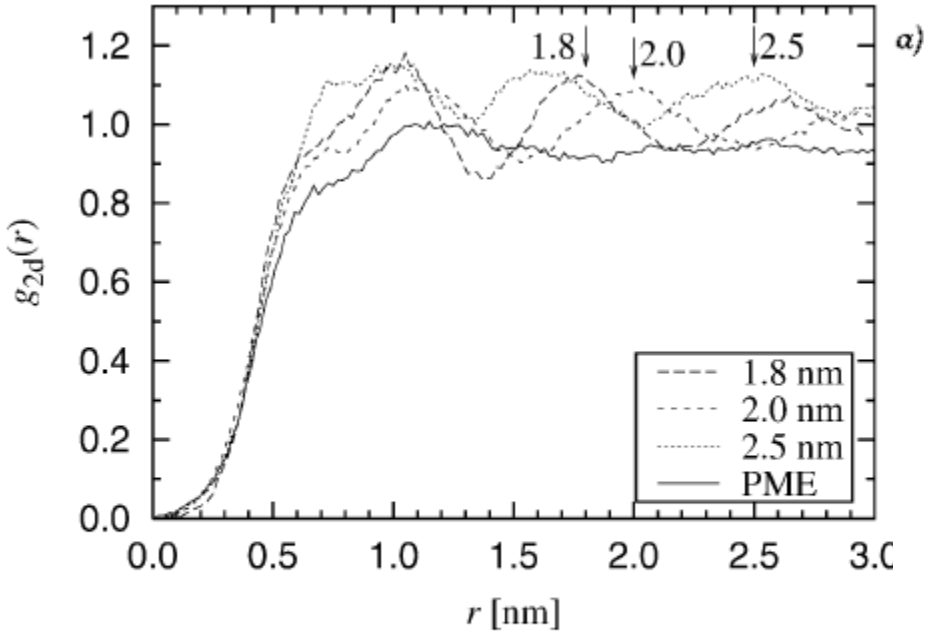
$$V_{\text{electrostatic}} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$ (Coulomb's law)



- Computationally, electrostatics poses a major challenge
  - long-ranged and decays as $1/r$
  - In general, we define a long-range interaction as one for which $V(r) \sim 1/r^a$, where $a < d$, and d is the dimension of space
- Cut-off, reaction-field, Ewald-type methods, multipole expansions, …

Effect of truncating electrostatic interactions in lipid bilayer: radial distribution function

Bare truncation of Coulomb interactions is likely to cause major error



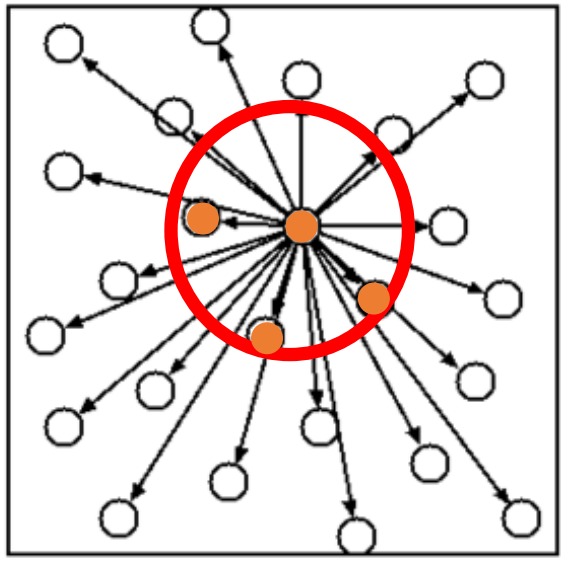


FIGURE 2 Radial distribution function $g_{2d}(r)$ for the center of mass positions of the DPPC molecules (Patra *et al.*, 2003).

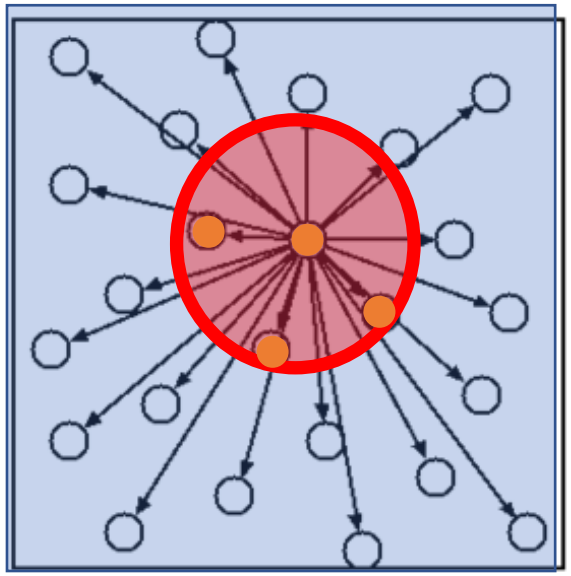
M. Patra et al., Biophys. J., 84:3636-3645, 2003

Reaction field electrostatics

- Explicit electrostatics with $r<r_{cut}$.
- For $r > r_{cut}$ the system is treated on a mean-field level and is thus completely described by its dielectric constant ε .

$$\mathcal{V}(r) = \frac{q_i q_j}{4\pi\epsilon_0 r}\left[1 + \frac{\epsilon - 1}{2\epsilon + 1}\left(\frac{r}{r_{\text{cut}}}\right)^3\right] - \frac{q_i q_j}{4\pi\epsilon_0 r_{\text{cut}}}\frac{3\epsilon}{2\epsilon + 1}, \quad \text{a)}$$

$$\text{for } r \leqslant r_{\text{cut}}.$$



Ewald summation

- Ewald converted 1927 the slowly, conditionally convergent sum for the Coulomb potential in infinite lattice into two sums that converge rapidly and absolutely, one in real space another in reciprocal space

$$\frac{1}{r} = \frac{f(r)}{r} + \frac{1 - f(r)}{r}$$

Ewald sum: periodicity

A.Y. Toukmaji, J.A. Board Jr. / Computer Physics Communications 95 (1996) 73–92

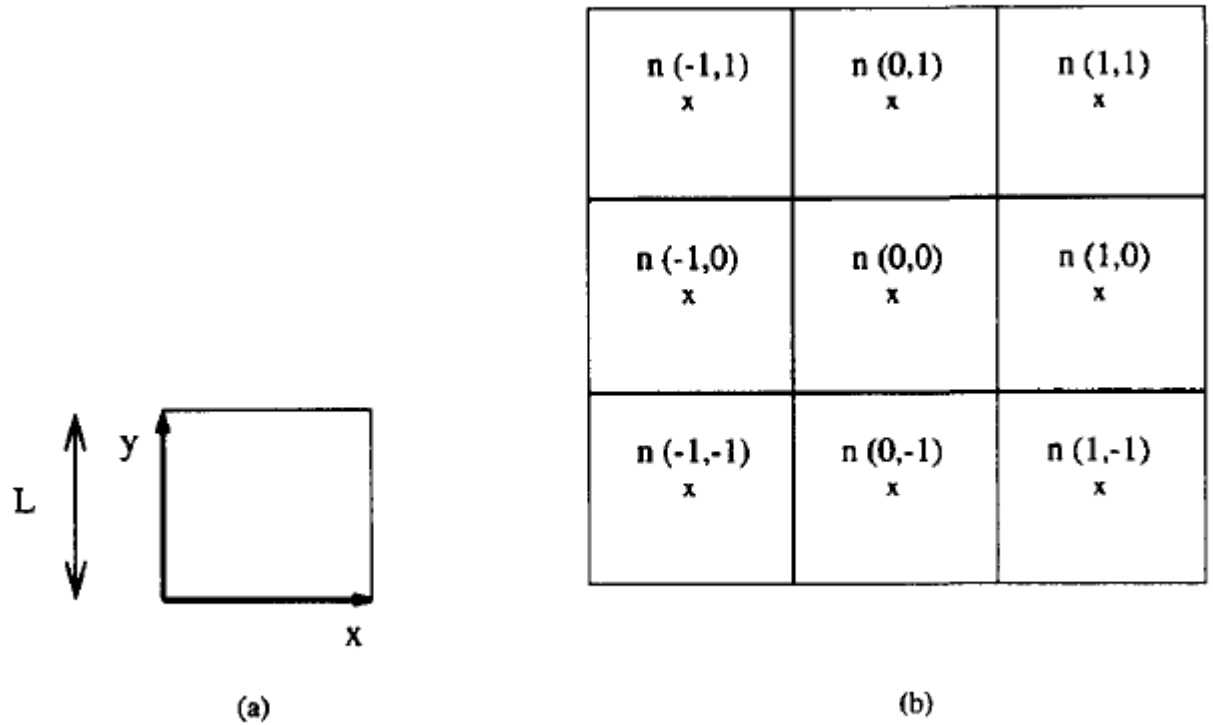


Fig. 1. In a 2D system (a) the unit cell coordinates and (b) a 3 × 3 periodic lattice built from unit cells.

Ewald sum

$$U = \frac{1}{2} \sum_{\boldsymbol{n}}' \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{q_i q_j}{r_{ij,\boldsymbol{n}}} ,$$

- $U_{Ewald}=U^r+U^m+U^0$
  - U^r Real space sum
  - U^m Reciprocal space sum
  - U^0 Constant term

n (-1,1) x	n (0,1) x	n (1,1) x
n (-1,0) x	n (0,0) x	n (1,0) x
n (-1,-1) x	n (0,-1) x	n (1,-1) x

$$U^r = \frac{1}{2} \sum_{i,j}^{N'} \sum_{\boldsymbol{n}} q_i q_j \frac{\operatorname{erfc}(\alpha r_{ij,\boldsymbol{n}})}{r_{ij,\boldsymbol{n}}} ,$$

$$U^m = \frac{1}{2\pi V} \sum_{i,j}^{N} q_i q_j \sum_{\boldsymbol{m} \neq \boldsymbol{0}} \frac{\exp(-(\pi \boldsymbol{m}/\alpha)^2 + 2\pi i \boldsymbol{m} \cdot (\boldsymbol{r}_i - \boldsymbol{r}_j))}{\boldsymbol{m}^2} ,$$

$$U^o = \frac{-\alpha}{\sqrt{\pi}} \sum_{i=1}^{N} q_i^2 .$$

V is the volume of the simulation box, $\boldsymbol{m} = (l, j, k)$ is a reciprocal-space vector, and $\boldsymbol{n}$ was defined earlier. The self-term U^o is a correction term that cancels out the interaction of each of the introduced artificial counter-charges with itself as will be explained in Section 2.2. The complimentary error function decreases monotonically as x increases and is defined by $\operatorname{erfc}(x) = 1 - \operatorname{erf}(x) = 1 - (2/\sqrt{\pi}) \int_0^x e^{-u^2} du$. The theory of Ewald summation is described in more detail by Kittel [33] and Tosi [51].

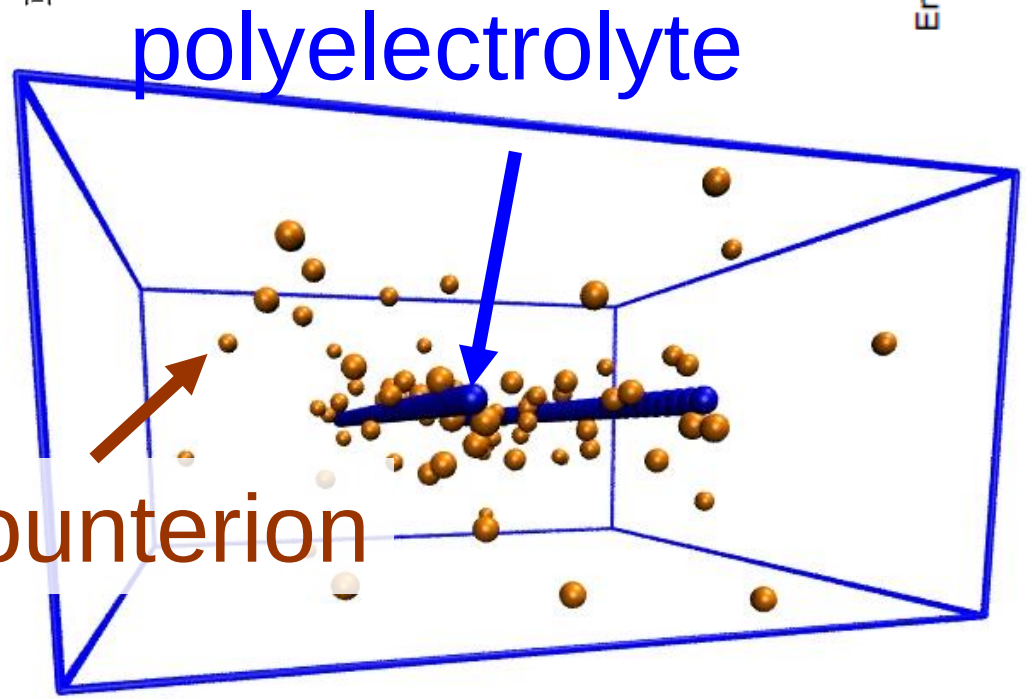
A.Y. Toukmaji, J.A. Board Jr./Computer Physics Communications 95 (1996) 73-92

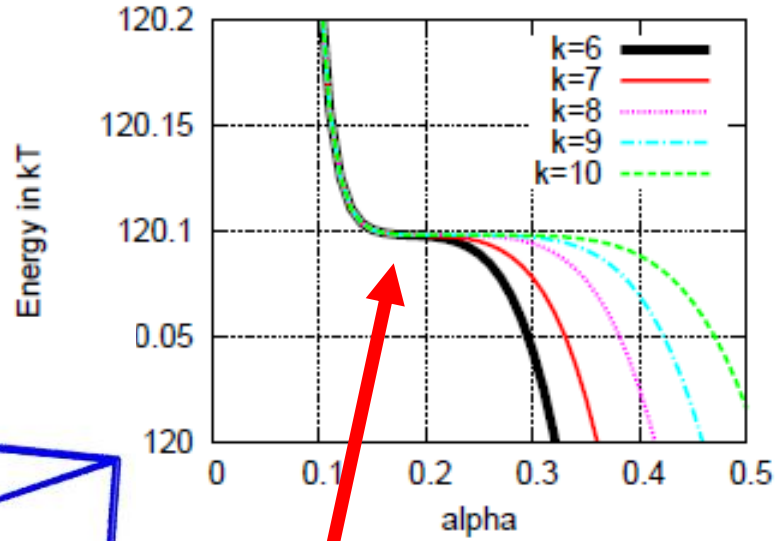
Ewald summation convergence: Example

$$U^r = \frac{1}{2}\sum_{i,j}^{N'}\sum_{\boldsymbol{n}} q_i q_j \frac{\operatorname{erfc}(\alpha r_{ij,\boldsymbol{n}})}{r_{ij,\boldsymbol{n}}},$$

$$U^m = \frac{1}{2\pi V}\sum_{i,j}^{N} q_i q_j \sum_{\boldsymbol{m}\neq\boldsymbol{0}} \frac{\exp(-(\pi\boldsymbol{m}/\alpha)^2 + 2\pi i\boldsymbol{m}\cdot(\boldsymbol{r}_i - \boldsymbol{r}_j))}{\boldsymbol{m}^2},$$

$$U^0 = \frac{-\alpha}{\sqrt{\pi}}\sum_{i=1}^{N} q_i^2 .$$





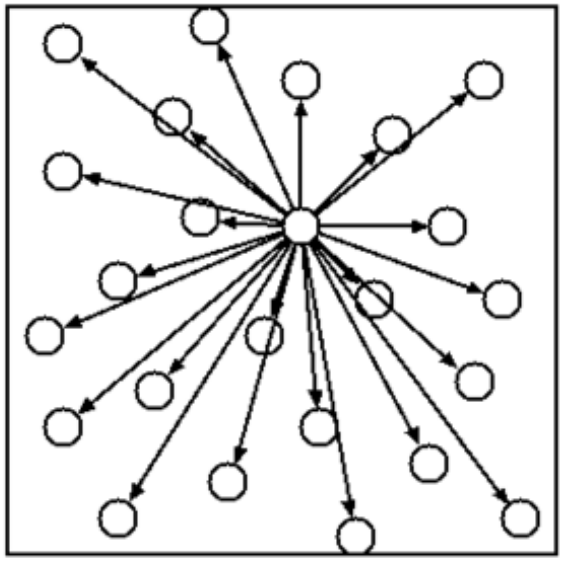
Convergence Region (plateau)

Cut-offs

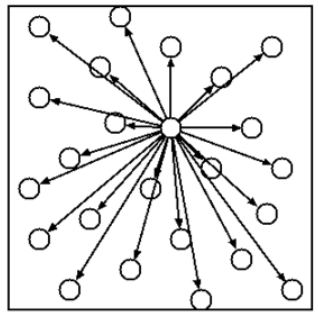
Cut-off schemes in calculating interactions

- Truncating the potential and neighbor lists
  - Bonded interactions have limited number of particles involved and scale as O(N) (N number of particles)
  - Non-bonded (in principle) interactions involve all combinations of N particles in an N particle system. Scales as $O(N^2)$. PROBLEM!

a)



Let's take a look at Lennard-Jones potential: Decays as r^{-6}

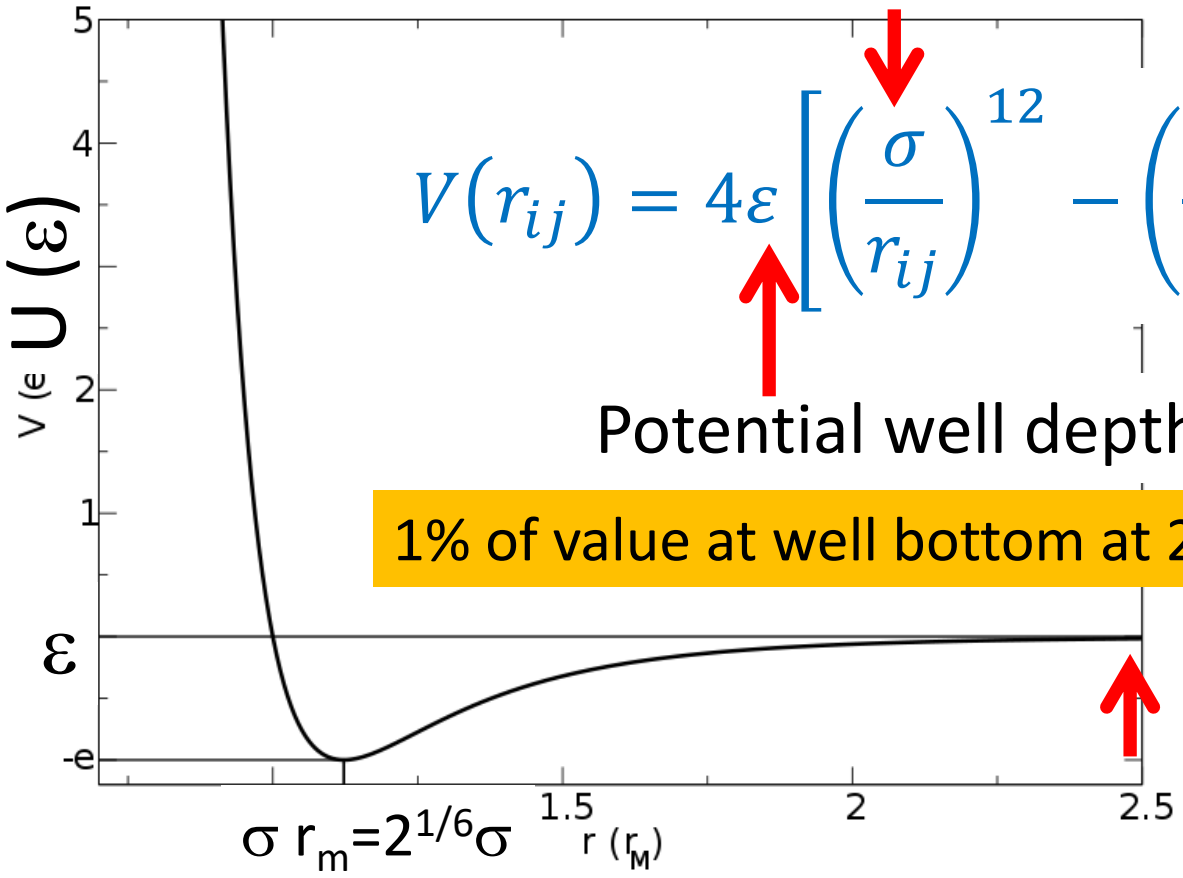


zero-separation

$$V(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

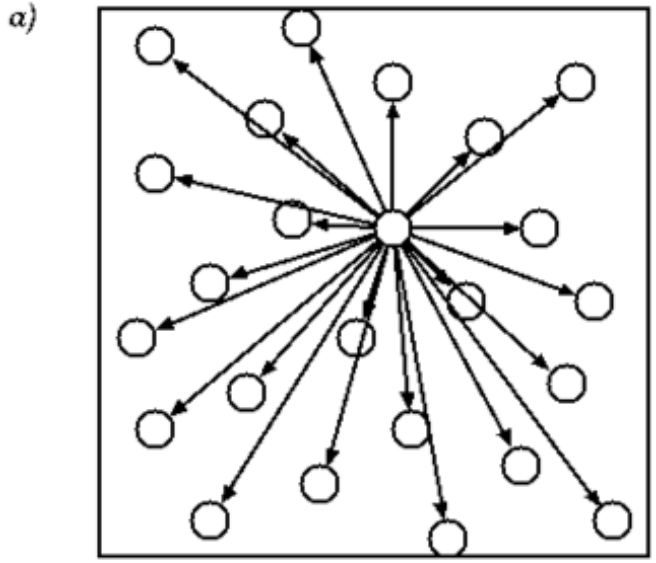
Potential well depth

1% of value at well bottom at 2.5σ separation



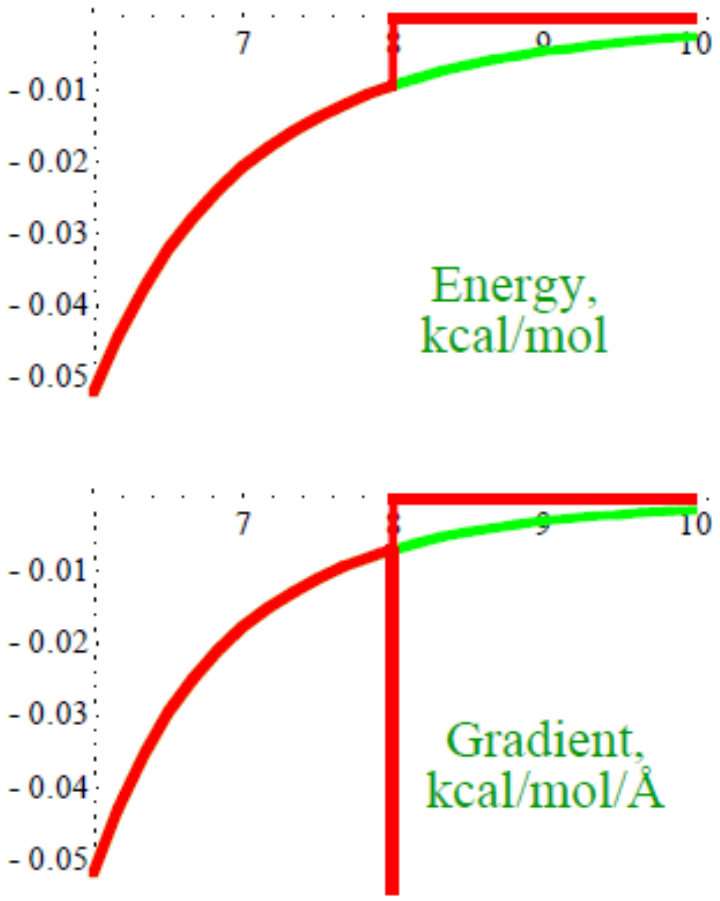
Cut-off schemes in calculating interactions

- Minimum image convention: at max ½ of smallest box side
- Lennard-Jones: 2.5σ corresponds to 1% error
- Coulombic interactions: any kind of cut-off has been shown to cause artifacts: Long range electrostatics such as PME of multipole expansions preferred, reaction field type methods use ~1nm switch cut-off
- More about long-range electrostatics later



Fine-tuning the truncation scheme

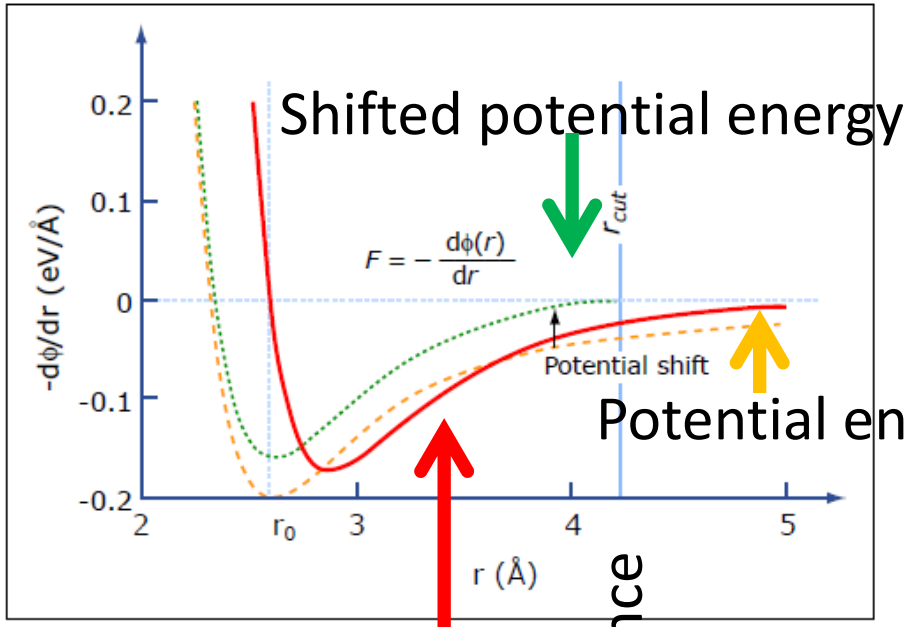
- Typically just cut-off, but discontinuity in energy / force may be problem
- To remove discontinuity energy function may be
  - shifted to zero at cut-off
  - switched to zero at cut-off (switching function)
- To remove force discontinuity, the derivative values may be modified at cut-off region



Fine-tuning the truncation scheme

- Potential shifted to zero at cut-off
  - $v'(r)=v(r)-v(r_{cut})$, $r<r_{cut}$
  - $v'(r)=0$, $r>r_{cut}$
  - Does not affect force
- Force has discontinuity at cut-off: drop from finite value to zero
  - Force discontinuity can be avoided by setting derivative zero at cut-off
  - $v'(r)=v(r)-v(r_{cut})-\left(\frac{dv(r)}{dr}\right)_{r=rcut}(r-rcut)$, $r<r_{cut}$
  - $v'(r)=0$, $r>r_{cut}$
  - May be complicated to implement in many body potentials

Fine-tuning the truncation scheme
Lennard-Jones as example of shifted potential



Fine-tuning the truncation scheme

- Potential switched to zero either over r< rcut or over a short region before rcut (switching function).
  - Switching function $v'(r)=v(r)S(r),\ r<r_{cut}$
  - $v'(r)=0,\ r>r_{cut}$
  - $S(r=0)=1\ \ S(r_{cut})=0$
  - Affects force
- Preferentially 1st and 2nd derivative values at onset of switching and at r_{cut} zero!! (No “jumps” in force)
- Correcting for switching function “jumps” critical in reactive force-fields

GROMACS

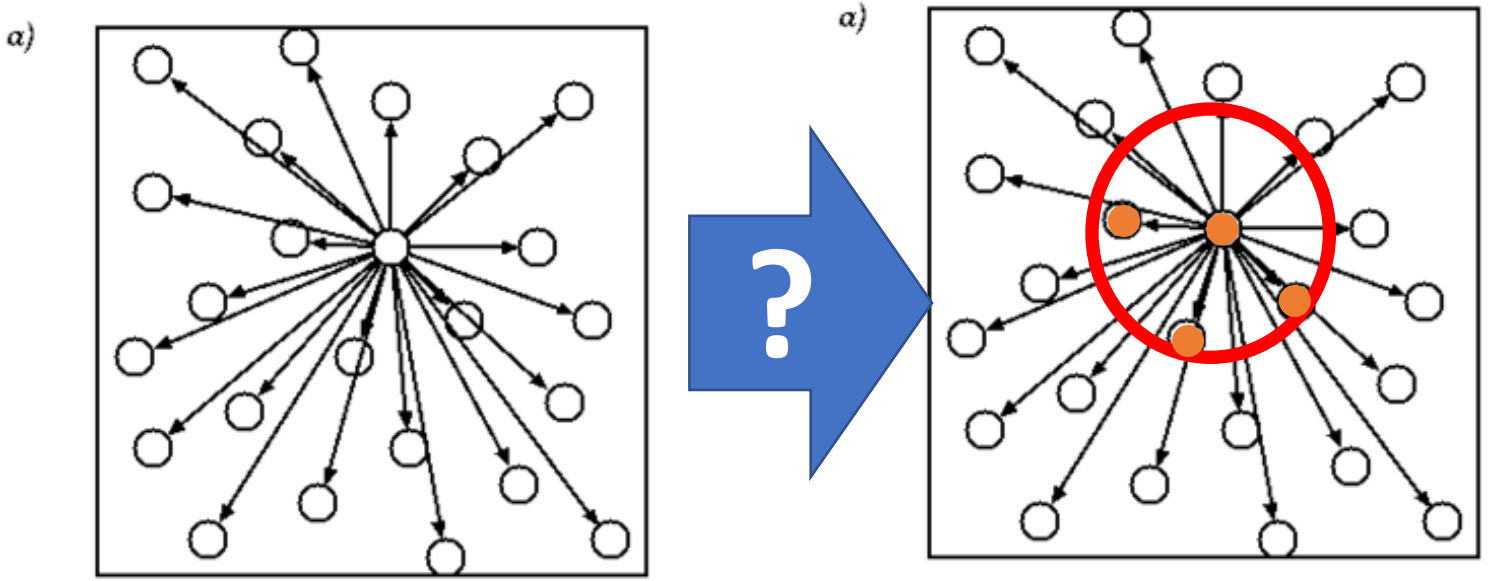
Truncation of LJ potential is specified in the run parameter file **mdp**.

File content

```
vdw-modifier = potential-shift
;  Shifts the VDW potential by a constant such that it is zero at the rvdw.

vdw-modifier = force-switch
;  Smoothly switches the forces to zero between rvdw-switch and rvdw.

vdw-modifier = potential-switch
;  Smoothly switches the potential to zero between rvdw-switch and rvdw.

vdw-modifier = none

rvdw-switch = 1.0
;  Where to start switching.

rvdw = 1.2
;  Cut-off distance
```

Computational efficiency: How to define which particles are interacting if there is a cut-off?

- If we need to calculate distances to all the particles (minimum image convention), the computational effort is almost as large as calculating all the energies without cut-off
- Most neighbors stay same on consequent steps
- How does one define, which particles are within cut-off distance of each particle?



Common solution: Verlet neighbor list

- For each particle i, a list of all particles j within cut-off distance r_{cut} + neighbor list skin thickness distance r_m
  - The list is updated only every M time steps
  - M and r_m-r_{cut} are chosen such that
- r_m-r_{cut}>Mvδt, where v is a typical atom velocity and δt the time step
- Update interval M can be 1) constant interval (simplest), 2) coupled to average v (better) or 3) coupled to maximum displacement of particles kept track with (best)